Journal of Industrial and Engineering Chemistry 57 (2018) 64–71

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Efficient biosorption of Pb(II) from aqueous solutions by a PAH-degrading strain *Herbaspirillum chlorophenolicum* FA1

Xiaohui Li[a], Hongxia Xu[a,*], Bin Gao[b], Xiaoqing Shi[a], Yuanyuan Sun[a], Jichun Wu[a,*]

[a] Key Laboratory of Surficial Geochemistry of Ministry of Education, School of Earth Sciences and Engineering, Hydrosciences Department, Nanjing University, Nanjing 210023, China
[b] Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, USA

ARTICLE INFO

Article history:
Received 13 January 2017
Received in revised form 21 July 2017
Accepted 4 August 2017
Available online 12 August 2017

Keywords:
Biosorption
Heavy metal
Pb(II)
Biosorbent
PAH-degrading bacterium

ABSTRACT

For the first time, biosorption of lead(II) using a PAHs-degrading bacterium, *Herbaspirillum chlorophenolicum* FA1, was investigated as a function of initial lead concentration, biomass dosage, pH, and temperature in batch conditions. Results showed that FA1 was highly resistant to lead and grew well even at lead concentration of 200 mg L^{-1}. The kinetic and isotherm data were well described by commonly used models, such as the pseudo-second-order and Langmuir models. Adsorption thermodynamics was spontaneous and endothermic, and FA1 exhibited a high sorption capacity of 151.52 mg g^{-1}. SEM-EDS and FTIR analysis was conducted to further explore the interaction mechanisms.

Introduction

The rapid worldwide industrialization has led to serious heavy metal pollution to the environment [1–4]. Unlike organic contaminants, heavy metals are not biodegradable and have strong tendency to accumulate in living organisms including human organs via food chains, threatening ecosystem and public health even at relatively low concentrations [5,6]. Lead (Pb) is one such toxic heavy metal that has been widely used in processing industries such as electroplating, paint and dyes, explosive manufacturing, and lead batteries [7,8]. It is regarded as one of the most concerned heavy metals because of its toxicity and wide spreading in terrestrial and aquatic environment [9]. In China, the annual output of lead has reached 135 million tons and more than 80 million tons have been consumed since 2004 [10]. The environmental exposures of lead due to indiscriminate dumping have posed serious health problems [11]. Hence, effective removal of lead from the environment is of great urgency and importance.

Various methods such as chemical precipitation, chemical oxidation and reduction, ion exchange, and adsorption are currently available for the treatment of heavy metals. While these methods have been and will continue to be widely applied, there are also associated disadvantages, such as high costs, low efficiency, and potential secondary pollution due to the generation of toxic sludge [5,12,13]. Therefore, search for other cost effective and efficient alternatives is necessary. Diverse studies have suggested that biosorption can be one of the most promising approaches towards the removal of heavy metals due to its environmental friendliness, high efficiency, cost effectiveness and the availability of large quantities [4,14–16].

There are considerable publications on the remediation of heavy metal pollution using various types of biosorbents, such as fruit waste (kernel, seed and peel) [8], agricultural waste [17], microorganisms include bacteria, fungi, and algae [18–20]. One important characteristic of biosorbents is that biomass used for sorption may be living or dead. For the majority of metal removal studies, the use of dead biomass or derived products seems to be a preferred alternative by reducing complexity, while many attributes of living microorganisms remain unexploited [21]. Recent few researches have demonstrated the effective removal of lead by living microbial cells of *Microcoleus* sp. [19], *Bacillus* sp. [4], *Phanerochaete chrysosporium* [22], and *Saccharomyces cerevisiae* [23]. The lead sorption abilities of these living microbial biosorbents were determined under the stress from the heavy metal alone. However, heavy metals often co-exist with organic contaminants like polycyclic aromatic hydrocarbons (PAHs) in the

* Corresponding authors at: Key Laboratory of Surficial Geochemistry of Ministry of Education, School of Earth Sciences and Engineering, Hydrosciences Department, Nanjing University, Xianlin Campus, Xianlin Boulevard 163, Nanjing 210023, China. Fax: +86 25 89680517.
E-mail addresses: hxxu@nju.edu.cn (H. Xu), jcwu@nju.edu.cn (J. Wu).

http://dx.doi.org/10.1016/j.jiec.2017.08.008
1226-086X/

polluted environment [24,25]. The bioremediation of heavy metals can be challenging in the presence of PAHs because they can cause severe toxic effect to the biosorbents. In this regard, live microorganisms that can tolerate or even degrade PAHs are preferred biosorbents for heavy metals.

For the first time, a PAH-degrading bacterial strain *Herbaspirillum chlorophenolicum* FA1 (*H. chlorophenolicum* FA1) was used as a biosorbent for the removal of lead from aqueous solution. Susceptibility of the bacterial strain under the Pb(II) stress was first determined. Batch sorption experiments were then conducted to obtain the sorption kinetics and isotherms of Pb(II) onto the living cells of targeted biosorbent. The effects of initial Pb(II) concentration, biomass dosage, temperature, and pH on the sorption of Pb(II) onto the biosorbent were also determined. The main objective of this work was to evaluate the ability and potential application of this novel PAH-degrading biosorbent as a remediation agent for treating Pb(II) pollution.

Materials and methods

Preparation of biosorbent and Pb(II) stock solution

H. chlorophenolicum FA1, a PAH-degrading bacterium deposited in the China General Microbiological Culture Collection Center with the accession number CGMCC3797, was isolated from activated sludge [26]. Strain FA1 was inoculated into sterile Luria–Bertani (LB) medium and cultured in a thermostatic shaker at 30 °C, 125 rpm. After incubation, the cells were harvested by centrifugation at 8000 rpm for 8 min at 4 °C when they grew to logarithmic growth phase, and washed three times with 150 mM NaCl solution. Afterwards, the cells were resuspended in NaCl solution for sorption experiments.

Stock solution of Pb(II) (1000 mg L^{-1}) was prepared by dissolving appropriate amount of $Pb(NO_3)_2$ in deionized (DI) water, and working concentrations of Pb(II) were obtained via serial dilution.

All glass and plastic ware and solutions were sterilized before experiments by autoclaving at 121 °C for 30 min.

Susceptibility of H. chlorophenolicum FA1 to different concentrations of Pb(II)

The microbial susceptibility of strain FA1 to Pb(II) was determined with the presence of $Pb(NO_3)_2$ at different concentrations (0, 10, 20, 50, 100, 200 mg L^{-1}) using established method [19,27]. The cultures added with Pb(II) were incubated in a thermostatic shaker in the dark at 125 rpm, 30 °C, and the cell density was measured based on absorbance (OD_{600} nm) [28]. For each heavy metal concentration, the experiments were performed in triplicate, and blanks were conducted as negative controls.

Biosorption experiments

Batch sorption experiments of Pb(II) onto strain FA1 were performed in 20 mL polyethylene centrifuge tubes, which were agitated in an isothermal shaker at 125 rpm.

Sorption kinetics were investigated with an initial Pb(II) concentration of 30 mg L^{-1}, and a biosorbent concentration of 60 mg L^{-1} at pH 5.5 and 30 °C. NaCl was added into solution at 150 mM to maintain constant osmotic pressure. Samples were taken periodically and immediately filtered through 0.22 μm pore size nylon membranes for residual Pb(II) analysis. The Pb(II) concentrations were determined using Atomic Absorption Spectrometer (AAS, Z-2000, Hitachi, Japan). Sorption isotherms were conducted under similar conditions except that initial Pb(II) concentrations varied from 0 to 200 mg L^{-1}. Samples were taken when equilibrium was reached and then filtered for measurement of residual Pb(II).

Effects of biomass dosage (60, 120, 180 and 240 mg L^{-1}) on the biosorption of Pb(II) (30 mg L^{-1}) were also studied at 30 °C and pH 5.5. The effects of different temperatures (20 °C, 25 °C, 30 °C and 35 °C) on the metal ions sorption by the biomass were determined at pH 5.5. To study the influence of pH, batch experiments were conducted at 30 °C with pH varying from 2.0 to 5.5. Solution pH was adjusted to the desired values using 0.1 mol L^{-1} HCl. In order to avoid uncertainty into the interpretation of the biosorption results, experiments were not performed at pH > 5.5 because precipitation of Pb(II) might occur at higher pH conditions. In both temperature and pH experiments, the initial concentration of Pb(II) was 30 mg L^{-1} and the biomass dosage was 60 mg L^{-1}.

Control sets were performed under the same conditions without addition of bacterial cells. All the sorption experiments were conducted in triplicates and the average values were calculated. The solid phase Pb(II) concentration was calculated with:

$$q = \frac{(C_0 - C)V}{m} \quad (1)$$

where q represents the amount of metal sorbed onto the biomass (mg g^{-1}); C_0 and C are the initial metal concentrations and the metal concentration at equilibrium (mg L^{-1}), respectively; V is the volume of the medium (L); and m is the amount of the biomass (g).

Characterization of pre- and post-sorption biosorbent

Scanning electron microscope (SEM) imaging coupled with energy dispersive X-ray spectroscopy (EDS) (S-3400N II, Hitachi, Ltd., Japan) were used to determine the sorption of Pb(II). The SEM samples were prepared according to procedures established by Mohamad et al. [29]. Fourier transform infrared (FTIR) spectrometer (NEXUS870, USA) was also adopted to characterize the surface functional groups of the pre- and post-sorption biosorbent. The FTIR samples were prepared by diluting the biosorbent to 5% in KBr and cast in disks for FTIR analysis [10].

Results and discussion

Effect of Pb(II) concentrations on cell growth

Cell growth of strain FA1 in Pb(II) solution of different concentrations are shown in Fig. 1. The inhibition on growth of

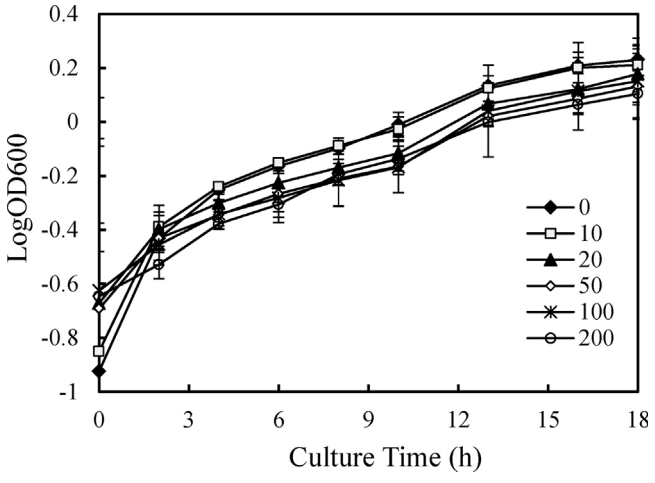

Fig. 1. Effect of initial Pb(II) concentrations on the growth of strain FA1.